FUNDAMENTALS OF HEAVY METAL REMOVAL BY DRY SORBENTS

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Abstract

Emission of toxic metal compounds is a major problem in many combustors and incinerators. In the present work, using cadmium chloride as a model compound, the use of solid sorbents for removal of toxic metal compounds from high temperature flue gases is investigated. The sorbents tested were silica, alumina, kaolinite, emathlite and lime. Compounds containing aluminum oxide show high cadmium removal efficiency. In particular, bauxite has the highest rate and capacity for cadmium capture. The overall sorption process is not just physical adsorption, but rather a complex combination of adsorption and chemical reaction.

Introduction

Cadmium compounds are considered to be among the most toxic trace elements emitted into the environment during fuels combustion and waste incineration. Cadmium and cadmium compounds are primarily used in the fabrication of corrosion resistant metals. Cadmium is also used as a stabilizer in poly-vinyl chlorides, as electrodes in batteries and other electrochemical cells, and for numerous applications in the semiconductor industry (1). Due to this wide range of applications, cadmium is present in many municipal and industrial wastes. Cadmium is also present in coal in trace quantities (2). Consequently, emission of cadmium compounds is a problem in many waste incinerators and coal combustors. The chemical form and concentration of these compounds depend on a number of factors including feed composition and operating conditions (3).

The increased use and disposal of cadmium compounds, combined with their persistence in the environment and relatively rapid uptake and accumulation in the living organisms contribute to their serious environmental hazards. The present technology is inadequate to meet the expected cadmium emission standards. Therefore, new and effective methods need to be developed and investigated for controlling the emission of cadmium and other toxic metals in combustors and incinerators.

A promising technique for the removal of metal vapors from high temperature gases is through the use of solid sorbents to capture and immobilize the metal compounds by a combination of adsorption and chemical reactions. The sorbent can be

used in two ways:

      a. It could be injected as a powder (similar to lime injection) for in-situ removal of cadmium compounds.

      b. The cadmium containing flue gas could be passed through a fixed or fluidized bed of sorbent. The sorbent could be used in the form of pellets, beads, or monoliths (for high dust applications).

Previous studies by us and other investigators indicate that solid sorbents can be very effective in removing alkali and lead vapors from hot flue gases (4-7). In the present work, a number of potential sorbents were screened and compared for their effectiveness in removing cadmium compounds from hot flue gases. Details of the sorption mechanism were investigated for the selected sorbents.

Experimental

Materials

In the first part of this study, several model compounds and naturally available materials were evaluated as potential sorbents for removal of gaseous cadmium compounds from hot flue gases. The model compounds included silica (MCB grade 12 silica gel) and alpha alumina (Du Pont Baymal colloidal alumina, technical grade). The naturally available materials included kaolinite (52% SiO_2, 45% Al_2O_3, 2.2% TiO_2, 0.8% Fe_2O_3), bauxite (11% SiO_2, 84% Al_2O_3, 5% Fe_2O_3), emathlite (73% SiO_2, 14% Al_2O_3, 5% CaO, 2.6% MgO, 3.4% Fe_2O_3, 1.2% K_2O) and lime (97% CaO). Cadmium chloride was used as the cadmium source. For the screening experiments, the sorbents were used in the form of particles, 60 - 80 mesh in size. For the kinetic and mechanistic study the sorbents were used in the form of thin flakes (disks). The flake geometry is easy to model and characterize using analytical techniques. All the sorbents were calcined at 900°C for two hours and stored under vacuum until used. All the experiments were conducted in a simulated flue gas atmosphere containing 15% CO_2, 3% O_2, 80% N_2 and 2% H_2O.

Equipment and Procedures

Screening Experiments: The main components of the experimental system were a Cahn recording microbalance, a quartz reactor, a movable furnace and analyzers for determining the composition of the gaseous products. This system has been previously used for screening of sorbents for removal of lead compounds. Therefore, only the salient features of the system are described here. Details can be found in a previous publication[4]. The cadmium source was suspended by a platinum wire from the microbalance, which monitored the weight change during the experiments. A fixed bed of the sorbent particles was made by placing 100 mg of the sorbent particles on a 100 mesh stainless-steel screen in a quartz insert. All experiments in this study were performed with the source at 560°C and the sorbent at 800°C. This method ensured that the concentration of cadmium vapors around the sorbent was much below saturation, thereby preventing any physical condensation on the outer surface of the sorbent.

Heating of the cadmium source resulted in vaporization of $CdCl_2$ which was carried by the flue gas through the sorbent fixed bed. The percentage of cadmium adsorbed was determined from the amount of cadmium delivered (microbalance measurement) and the cadmium content of the sorbent at the end of the experiment. The cadmium content of the sorbent was determined by dissolving the samples in a $H_2O/HF/HNO_3$ (2/1/1 proportion by volume) mixture and subsequently analyzing the solution by atomic absorption spectroscopy. Separate water leaching experiments were performed to determine the water soluble fraction of adsorbed cadmium. The leaching of cadmium was conducted at 40°C in an ultrasonic bath for two hours. The cadmium content of the solution was subsequently determined by atomic absorption spectroscopy.

Study of Sorption Details: A microbalance reactor system was used for studying the sorption details. The sorbent flakes were suspended by a platinum wire from the microbalance. The weight of the sorbent was continuously monitored during the experiments by the microbalance. The cadmium source was placed in the horizontal arm of the reactor. The simulated flue gas from the gas preparation section was split in two parts. One part entered the reactor from the inlet below the balance and the remaining gas entered through the horizontal arm in which the cadmium source was placed. The cadmium source was heated by a heating tape and a furnace heated the sorbent flakes. All experiments were conducted with the source temperature of 560°C and the sorbent temperature of 800°C. When steady flow rates and cadmium concentrations were achieved, the sorbent was exposed to the cadmium containing flue gas. The sorbent weight was continuously recorded as it captured the cadmium vapors. The microbalance was continuously purged with ultra high purity nitrogen gas.

Results and Discussion

Screening Experiments

The results obtained from the screening experiments are given in Figure 2. Multiple experiments were conducted for most of the sorbents and good reproducibility was obtained. Since all experimental parameters except the sorbent type were kept constant, the amount of cadmium adsorbed is a good indication of the sorbent effectiveness (rate) for cadmium removal from hot flue gases. The most obvious feature of these results is the difference in the ability of the sorbents to capture cadmium from the flue gas passing through them. Alumina and bauxite had the highest cadmium capturing efficiencies. A large fraction of the cadmium captured by these two sorbent was water insoluble. Silica and kaolinite were not effective for removal of cadmium. Since cadmium chloride has a high water solubility, the formation of water insoluble compounds on sorption by alumina and bauxite leads to the conclusion that chemical reaction is the dominant mechanism of cadmium capture by these sorbents. Lime, a sorbent used for removal of sulfur compounds, did not have a high cadmium capturing efficiency. Since most of the cadmium captured by lime was water soluble, physical condensation is the dominant mechanism of cadmium capture for lime. From the screening experiments, it seems that compounds containing aluminum oxide have a

high cadmium capturing efficiency. Bauxite was therefore further studied to determine the mechanism of cadmium capture. Since previous studies have indicated that kaolinite is a good sorbent for removal of lead and alkali compounds, it was also included in the mechanistic study.

Details of the Sorption Process:

In the first part of this study, the cadmium sorption capacity of kaolinite and bauxite was investigated at 800°C. In these experiments the sorbent flakes were exposed to cadmium vapors until no further mass change was observed. The profiles for sorption for both kaolinite and bauxite are shown in Figure 3. The rate of sorption decreases with time and a final limit is achieved beyond which no further cadmium sorption takes place. The observed initial rate for cadmium capture by kaolinite was much slower than that for bauxite. This is consistent with the results from the screening experiments, where kaolinite captured much less cadmium compared to bauxite. Also, the final saturation limit for kaolinite (18%) was found to be lower than that for bauxite (30%) (Figure 3). When the concentration of cadmium in the flue gas wa reduced to zero, no desorption from either sorbent was observed indicating that reversible physical adsorption was not the dominant sorption mechanism.

X-ray diffraction (XRD) analysis was used to identify the final products formed by sorption of cadmium chloride on kaolinite and bauxite. Analysis of kaolinite flakes exposed to cadmium vapors indicated the formation of a cadmium aluminum silicate compound, $CdAl_2Si_2O_8$, which is water insoluble. Based on XRD results, the following reaction scheme is proposed for capture of cadmium :

$$Al_2O_3.2SiO_2 + CdCl_2 + H_2O \quad \text{----} \quad CdO.Al_2O_3.2SiO_2 \; + \; 2HCl \quad (1)$$
metakaolinite
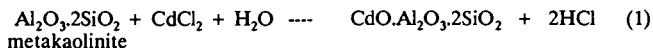
where metakaolinite is the dehydration product of kaolinite. Holland et al. (8) also observed the formation of this compound when a solid mixture of cadmium carbonate and kaolinite was heated to 800°C for twenty hours. Based on the stoichiometry of the overall reaction, 1 kg of kaolinite can capture 0.51 kg of cadmium, forming a product which is water insoluble and therefore safely disposable. The maximum weight gain postulated from this reaction (58% by weight) is much higher than that obtained experimentally in the microbalance reactor setup (18 wt%).

To further understand the reasons for low sorbent utilization, a kaolinite flake which had captured cadmium to its maximum capacity was mounted in epoxy and analyzed by SEM and EDX analysis. A cadmium map of the flake shows that cadmium is concentrated on the kaolinite edge (Figure 3). An EDX line scan on the flake surface indicated that the concentration of cadmium varied from 49 wt% at the edge to 2 wt% at the center. The concentration of cadmium at the edge (49%) is close to the value calculated from the postulated reaction mechanism assuming complete conversion (51%). This indicates that the surface of kaolinite was completely converted by reaction to form a cadmium aluminosilicate. Silicon and aluminum maps on the kaolinite surface indicate complete uniformity of distribution of these elements on the kaolinite surface. Since this flake had captured cadmium to its maximum capacity (microbalance data, Figure 3), the non-uniform distribution of cadmium indicates incomplete sorbent

utilization. Since the volume of the cadmium aluminosilicate phase is higher than that of the aluminum silicate phase, the formation of cadmium aluminum silicate at the outer surface probably blocks the sorbent pores, resulting in incomplete sorbent utilization.

XRD analysis of bauxite particles exposed to cadmium vapors indicated the formation of two crystalline compounds: a cadmium aluminum silicate and a cadmium aluminate. Since the cadmium aluminate has a higher water solubility compared to that of the aluminosilicate, bauxite has a larger fraction of water soluble cadmium in the screening experiments. The amount of SiO_2 present in bauxite is not enough to combine with all Al_2O_3 to form an aluminosilicate compound. Based on the stoichiometry of Reaction 1 and the amount of SiO_2 present, 1 kg of bauxite can capture 0.10 kg of cadmium to form a cadmium aluminosilicate. Based on the remaining alumina, 1 kg of bauxite can capture 0.94 kg of cadmium oxide forming a cadmium aluminate according to the following reaction mechanism:

$$Al_2O_3 + CdCl_2 + H_2O \ ---- \quad CdO.Al_2O_3 \ + \ 2HCl \tag{2}$$

If all the alumina and silica reacted with kaolinite to form cadmium aluminum silicate and cadmium aluminate (Reactions 1 and 2), the maximum weight gain possible is 1.06 kg per kg of bauxite. This is higher than the value obtained in the microbalance experiments conducted to completion (0.30 kg/kg bauxite).

To further understand the sorption mechanism, a bauxite flake exposed to cadmium vapors to the point of "no further weight change" was mounted in epoxy and analyzed by SEM and EDX analysis. The cadmium map on the bauxite surface indicated a non-uniform cadmium distribution (Figure 4). Comparison of the cadmium map with the aluminum and silicon maps on the flake surface indicated that regions high in both alumina and silica have high concentrations of cadmium. As confirmed by the XRD analysis, the cadmium present in the alumina phase reacts to form a cadmium aluminate. Regions rich in both alumina and silica combine with cadmium to form a cadmium aluminum silicate. EDX analysis of regions high in both aluminum and silicon indicated that the cadmium concentration was 26 wt%. EDX analysis of regions high in alumina indicated that the cadmium concentration in this phase (11 wt%) was much lower than that postulated by Reaction 2. This indicates that the alumina phase does not completely react with cadmium to form a cadmium aluminate. This could be due to the alumina phase having low porosity thereby preventing complete sorbent utilization. Also, formation of a higher volume product on the outer surface could inhibit further capture of cadmium.

From the mechanistic study it is clear that the sorption process under present experimental conditions is influenced by diffusional resistances. In practical systems, the rate of sorption can be increased by optimization of the sorbent pore structure to facilitate intraphase transport of cadmium vapors into the sorbent. The interphase mass transport limitations can also be reduced to increase the overall sorption rate.
For in-situ applications, the efficiency of the sorbent can be increased by decreasing the particle size.

Conclusions

1. Bauxite and, to a lower degree, kaolinite are effective sorbents for removal of cadmium in combustors and incinerators.

2. The sorption mechanism and the nature of final products formed have important implications in the way each sorbent may be used. Compared to kaolinite, bauxite has a higher sorption rate and capacity; however, the products of sorption in bauxite are more water soluble. Therefore, kaolinite is more suitable when no leaching from the spent sorbent can be permitted.

3. The overall sorption process is a complex combination of adsorption, condensation, diffusion and chemical reactions.

4. In adsorbing cadmium chloride, chlorine is not retained by either kaolinite or bauxite. Additional cleanup steps may be needed in systems where the presence of chlorine in the flue gas cannot be tolerated.

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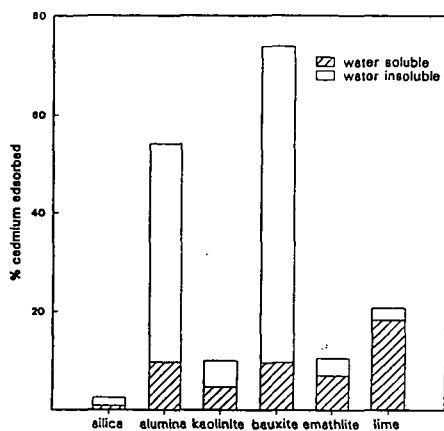(8)   Holland, A.E.; Segnit, E.R.; Gelb, T. Journal of The Australian Ceramic Society **1976**, 10, 1.

Figure 1: Cadmium removal efficiencies of various sorbents. Mass of sorbent used = 100 mg. T = 800°C. Amount of cadmium vaporized in each experiment = 6.5 mg.
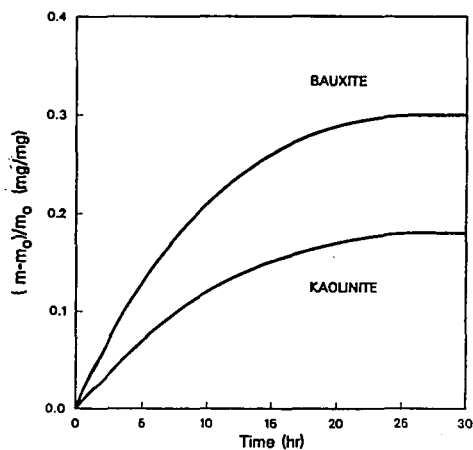

Figure 2: Temporal profiles of cadmium sorption on kaolinite and bauxite. T = 800°C. Flow rate = 200 cc/min. Mass of flake = 15.1 mg (bauxite); 20.4 mg (kaolinite). Flake thickness = 0.71 mm (bauxite); 1.1 mm (kaolinite)
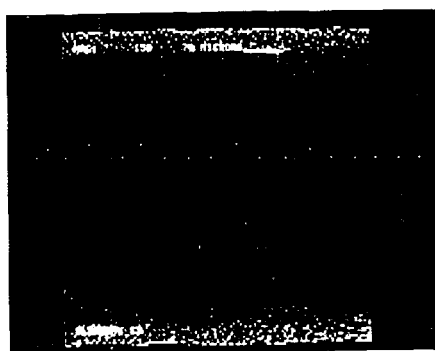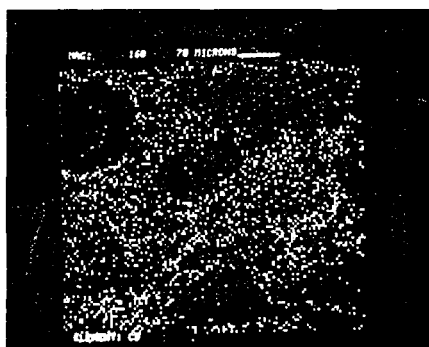
Figure 3: Cadmium concentration map on kaolinite flake surface

Figure 4: Cadmium concentration map on bauxite flake surface.